Bull. Chem. Soc. Ethiop. **1997**, 11(2), 145-150.
Printed in Ethiopia

ISSN 1011-3294

SENSITIZATION OF SINGLET OXYGEN ($^1\Delta_gO_2$) BY USE OF FÖRSTER ENERGY TRANSFER

Francis W. Maloba[a*], Michael L. Rooney[b], Paul Wormell[c] and Minh Nguyen[c]

[a]Chemistry Department, Kenyatta University, P. O. Box 43844, Nairobi, Kenya; [b]CSIRO Division of Food Science and Technology, North Ryde, NSW 2113, Australia; [c]Faculty of Science and Technology, University of Western Sydney, Hawkesbury, Richmond, NSW 2753, Australia.

(Received February 12, 1997; revised September 18, 1997)

Abstract. Quenching of curcumine fluorescence by thionine, both immobilised in cellulose acetate occurs in accordance with the Förster mechanism of energy transfer. The rate constant of energy transfer for this donor - acceptor pair is found to be 9.4 x 10^9 L^{-1} mol s^{-1} with $R_0 = 37\pm1$ Å. When this donor - acceptor pair is excited in the presence of oxygen, singlet oxygen ($^1\Delta_gO_2$) is also produced as a consequence. The application of this process of singlet oxygen sensitization for scavenging of oxygen is demonstrated.

INTRODUCTION

In previous studies on energy transfer, it has been shown that energy transfer takes place between a food dye curcumine as energy donor (D^*) and a thiazine dye methylene blue as harvester (X) [1, 2] in a manner consistent with the following Förster equation for long range energy transfer [3-7].

$$k_{D^* \to X} = \frac{8.8 \times 10^{-25} K^2 \Phi_D}{n^4 \tau_D R^6} \int_0^\infty \frac{F_D(\bar{v}) \epsilon_x(\bar{v}) d(\bar{v})}{\bar{v}^4} \qquad (1)$$

where the terms take their usual meanings [2, 4]. When this process is carried out in oxygenated matrices using good singlet oxygen sensitizers as energy harvesters, singlet oxygen is produced [1,2]. This may be confirmed from the photodegradation of suitable acceptors of singlet oxygen and by simple physical quenching studies [1, 2].

This paper reports on further studies on long range energy transfer between curcumine as donor and another thiazine dye, thionine, which is closely related to methylene blue as energy harvester (Figure 1). Since thionine is known to have a higher quantum yield of singlet oxygen sensitization than methylene blue [8], it is believed that excitation of this dye by energy transfer should result in faster photodegradation of a singlet oxygen acceptor, 2,5-diphenylfuran [9].

Different approaches for studying the energy transfer phenomenon are adequately described in the literature [2, 3-7, 10-13]. For the donor and acceptor immobilised in a plastic film, one simple approach and the one which was used in this work involves measuring the quenching of donor fluorescence quantum yields by varying amounts of a fluorescence quencher [13]. The rates of energy transfer are then calculated from the following Förster's

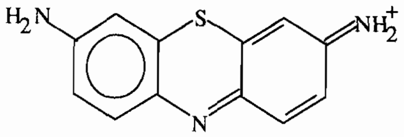

Figure 1. Molecular structure of Thionine (Th).

derived luminescence equation [3, 7].

$$\frac{\Phi_X}{\Phi_o} = 1 - \sqrt{\pi} x e^{x^2}(1 - erf(x)) \qquad (2)$$

where the terms are described as before [1, 2].

EXPERIMENTAL

Materials. Thionine (Th) (BDH Analar) was crystallised from ethanol and dried in the oven at 105 °C. The other reagents curcumine (CUR) (laboratory reagent), rhodamine B (RhB) (Spot test reagent, C. I. 45170), perchloric acid (High quality spectro grade), sodium nitrite (BDH Analar), 2,5-diphenylfuran (DPF) (BDH Analar), cellulose acetate (Ajax Chemicals) and the Reinecke's salt, $K(Cr(NH_3)_2(NCS)_4$, that was used in actinometry were treated as described before [1]. The solvents chloroform, absolute ethanol and acetone (BDH Analar) were used as received.

Sample preparation. Stock solutions of CUR (5 x 10^{-3} M) and Th (10^{-2} M) were prepared in ethanol and that of DPF (0.1 M) was made in chloroform. Cellulose acetate (CA) polymer films were cast under dim light in the dark room on a K-coater RK Print coat (Unit No. 41889) [2]. Sample films consisted of 10^{-3} M CUR and varying amounts of Th.

Spectrofluorimetry. The fluorescence spectra were recorded at ambient temperature (23°) on a Perkin Elmer MPF 44B fluorescence spectrophotometer. Fluorescence quantum yields were obtained from corrected spectra on the basis of RhB ($\Phi = 0.93$) using a standard procedure [1, 2, 14].

Absorption spectra and light exposure. Absorption spectra were recorded on a Perkin Elmer Lambda 2 UV/VIS spectrophotometer interfaced to an Amstrad 20 MB, 640 K personal computer. Samples were irradiated with an Osram HBO 200 W super pressure mercury lamps, housed in a Bausch and Lomb SP 200 lamp holder attached to a Bausch and Lomb high intensity monochromator (Cat. No. 33-86-76). The details of how the irradiations were done have already been described [1, 2].

RESULTS AND DISCUSSION

Figure 2 shows the emission and absorption spectra of CUR and Th. The emission spectrum of CUR (normalised at 520 nm) overlaps with the absorption spectrum of Th with the overlap integral of 4.7 x 10^{-13} (equation (1).

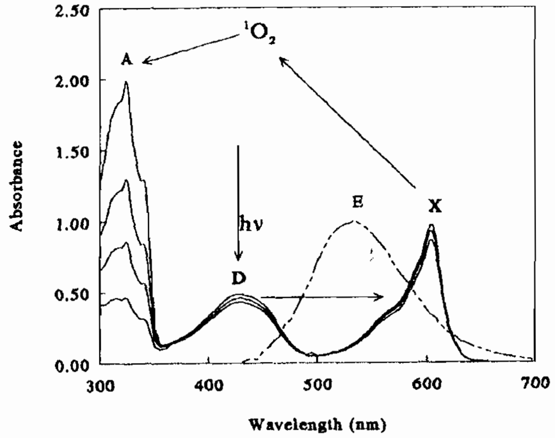

Figure 2. The absorption spectra of CUR (*D*), Th (*X*), DPF (*A*) and the emission spectrum of CUR (*E*).

Table 1. Quenching of curcumine (Cur) fluorescence by Thionine (Th) in 20 µm cellulose acetate films.

[Cur] / M	[Th] / M	Φ_X/Φ_0	P_{D^*A}	x	R_0 (Å)
10^{-3}	0	1.00	-	-	-
10^{-3}	1 x 10^{-3}	0.83	0.17	0.11	36
10^{-3}	2 x 10^{-3}	0.61	0.39	0.30	39
10^{-3}	3 x 10^{-3}	0.51	0.49	0.42	38
10^{-3}	4 x 10^{-3}	0.42	0.59	0.57	38
10^{-3}	5 x 10^{-3}	0.37	0.63	0.66	37
10^{-3}	6 x 10^{-3}	0.34	0.66	0.71	36

The mean experimental value of $R_0 = 37\pm1$ Å.

CUR when immobilised in this film fluoresces with a quantum yield of 0.25±0.05 [1, 2]. Table 1 shows the results for quenching of CUR fluorescence by thionine in cellulose acetate film. The R_0 values were derived from quantum yields by evaluating the error function in equation (2) using tabulated values [15] in conjunction with a fixed point iteration method.

From this Table, one observes that the derived R_0 value is constant at 37±1 Å with a probable error of 3%, even with variation of the harvester concentration. This variation is a reasonable estimate of experimental statistical error. From the overlap integral, it can be calculated that R_0 = 42 Å. This is in agreement with the experimentally determined value, and is also larger than the normal collisional distances (10-15 Å). When this experimental R_0 value is substituted in equation (1), the rate of energy transfer is found to 9.4 x 10^{10} L mol^{-1} s^{-1}. This K_{et} value compares well with the value for methylene blue [1] and is within acceptable

Table 2: Quantum yields for CUR-Th sensitized photooxidation of 3 x 10^{-2} M DPF in 20 µm cellulose acetate films.

[Th]/10^{-3} M	Φ_{DPF}
0.00	0.25
0.60	0.28
0.80	0.30
1.00	0.33
2.00	0.38
3.00	0.40
4.00	0.51
5.00	0.54

Φ_{DPF} = quantum yield for DPF photodegradation; * relative error = 5%

levels for the rate of a second order light process. This coupled with sensitized fluorescence of Th as CUR fluorescence is quenched confirms that energy transfer takes place by a long range Förster mechanism [2, 3].

Thionine is a known good sensitizer of singlet oxygen [8]. Curcumine on the other hand has a quantum yield of only 0.036 in solution [1]. Immobilization of a dye in a film is known to enhance the formation of the triplet state which in turn favours Type II reactions leading to singlet oxygen production. Thus, in Table 2, curcumine in cellulose acetate film sensitizes the photodegradation of a singlet oxygen acceptor DPF (k_r = 9 x 10^{7} L mol^{-1} s^{-1}) with a yield of 0.25. When thionine (ϵ = 557 L mol^{-1} cm^{-1} at 430 nm) is added to the film together with curcumine and irradiated at the curcumine maximum peak (ϵ = 49000 L mol^{-1} cm^{-1} at 430 nm) one observes that the quantum yield for photodegradation of DPF increases with increasing quenching of curcumine excitation. One expects that broad band irradiation of these two dyes would enhance the rate of photodegradation of DPF even further.

Further evidence of singlet oxygen production is provided by quenching of singlet oxygen with a known physical quencher of singlet oxygen, sodium azide [2]. In accordance with the known kinetics of this physical quenching of singlet oxygen [16], Figure 3, shows plots of [DPFO$_2$]$^{-1}$ *versus* [DPF]^{1} which are linear, with same intercepts but with different slopes. This is adequate evidence that the intermediate species in the photooxidation of DPF by this method of sensitization is singlet oxygen [16].

The enhancement of singlet oxygen production as observed here has important implications for enhancing processes that proceed via singlet oxygen generation. An example of such a process is the polymer bound oxygen scavenging [9, 17-19]. This novel development involves immobilization of suitable dyes and singlet oxygen acceptors in a suitable film base. By appropriate excitation of the dye, a sequence of reactions are set up that ultimately lead to the production of singlet oxygen, which in turn chemically binds onto a singlet oxygen acceptor, such as the furan compound used here. A simplified photochemical sequence is as follows.

$$D + h\nu \rightarrow {}^1D$$
$${}^1D \rightarrow {}^3D$$
$${}^3D + {}^3\mathrm{O}_2 \rightarrow D + {}^1\mathrm{O}_2$$
$${}^1\mathrm{O}_2 + A \rightarrow A\mathrm{O}_2$$

where *D* is for a dye while *A* stands for a singlet oxygen acceptor such as DPF used here. The

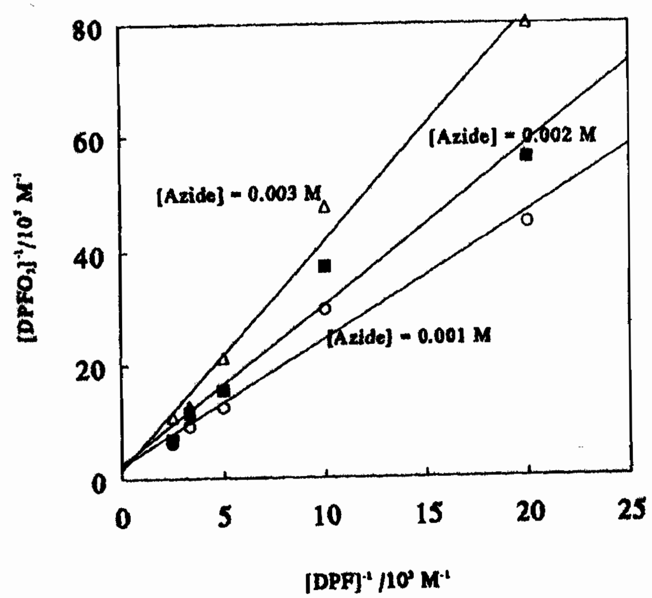

Figure 3. Quenching of the CUR-Th energy transfer sensitized photooxidation of DPF by NaN_3 in cellulose acetate films.

superscripts 1 and 3 stand for the singlet and triplet states respectively.

When this process is initiated while the film is in an oxygen impermeable package, it has been shown by several workers [2, 9, 17, 19] that it is possible to deoxygenate the package, thus creating an inert atmosphere which is necessary in such areas as packaging of oxygen sensitive foods, chemical reactors and essences.

Recently we managed to synthesize a highly concentrated singlet oxygen acceptor polyfuryloxirane (PFO) [2]. This polymer was used in conjunction with polychromatic light to scavenge oxygen from 200 mL of air inside PVDC-coated polypropylene pouches (of dimensions 23 cm x 17 cm). The results in Figure 4 show that films consisting of thionine scavenge oxygen faster than those consisting curcumine, and when both dyes are immobilised in the same film, the rate of scavenging oxygen is higher. We have shown before that increase in dye concentrations above 10^{-3} M does not lead to a proportional increase in the rate of scavenging [2, 19]. In some cases, this may lead to reduction in the rate of oxygen scavenging. It therefore means that the observed enhancement in scavenging when both dyes are in the same film is due to energy transfer. In another novel related development, this polyfuryloxirane film was used in enhancing the shelf life of sunflower oil [9].

This system has not been optimised. Besides, toxicity studies on the polyfuryloxirane film need to be undertaken. It is also believed that by using this process of dye sensitization, other processes that proceed via singlet oxygen sensitization such as photodynamic therapy, polymer photodegradation and stabilization, can in principle be enhanced [2]. It is in this direction that further studies in this area are being undertaken.

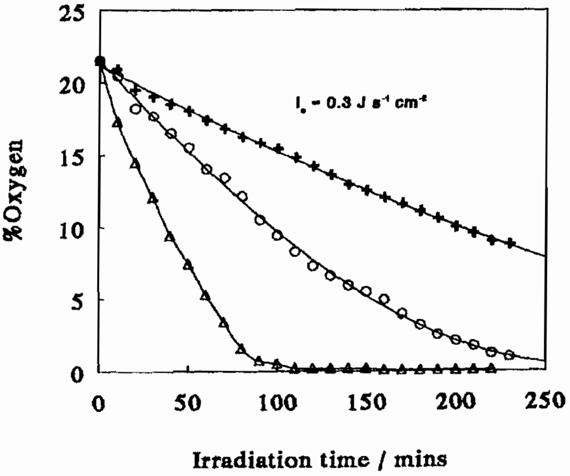

Figure 4. Scavenging of oxygen from PVDC-coated polypropylene pouches with PFO following sensitization by 10^{-3} M CUR (+); 10^{-3} M Th (o); 10^{3} M CUR and 10^{3} M Th (Δ).

REFERENCES

1. Maloba, F. W. *Bull. Chem. Soc. Ethiop.* **1996**, 10, 9.
2. Maloba, F. W. *Ph.D Thesis*, University of Western Sydney (Australia) 1994.
3. Förster, T. H. *Discussions Faraday Soc.* **1959**, 27, 7.
4. Förster, T. H. in *Modern Quantum Chemistry*, Part IIB, Light and Organic Crystals; O. Sinanoglu (Ed.), Academic Press: New York; 1965; p 93.
5. Lamola, A. A. *Techniques of Organic Chemistry*, Vol. 14, Leermakers, P. A.; Weissberger, A. (Eds.), John Wiley: New York; 1969; p 7.
6. Turro, N. J. *Modern Molecular Photochemistry*, Benjamin: Menlo Park; 1978; Ch. 9.
7. Berkovic, G. *J. Chem. Educ.* **1984**, 61, 832.
8. Usui, Y. *Chem. Lett.* **1978**, 743.
9. Maloba, F. W.; Rooney, M. L.; Wormell, P.; Nguyen, M. *J. Am. Oil Chem. Soc.* **1996**, 73, 181.
10. Parker, C. A.; Rees, W. T. *Analyst* **1960**, 85, 574.
11. Demas, J. N. *Excited State Lifetime Measurements*, Academic Press: London; 1983.
12. Bennett, R.G. *J. Chem. Phys.* **1964**, 41, 4048.
13. Turro, N. J. *Molecular Photochemistry*, W. A. Benjamin: San Francisco; 1965; Ch.5.
14. Ferreira, L. F.; Silvia, M. B.; and Pereira, E. J. *J. Photochem. Photobiol. A. Chem.* **1991**, 55, 361.
15. Abramowitz, M.; and Stegun, I. *A Handbook of Mathematical Functions*, Dover: New York; 1970.
16. Zweig, A.; Henderson, W. A. Jr. *J. Poly. Sci. Poly. Chem. Ed.* **1975**, 13, 717.
17. Rooney, M. L. *Chem. Ind.* **1982**, 20, 197.
18. Rooney, M. L.; Maloba, F. W.; Nguyen, M.; and Wormell, P., *Abstract*, AIFST, National Convention Centre: Canberra; 1994.
19. Rooney, M. L.; Holland, R. V.; Shorter, A. J. *J. Sci. Food. Agric.* **1981**, 32, 265.